9 Micelles, Vesicles, and Bilayers

9.1 Thermodynamics of Self-Assembly

Amphiphilic substances are dissolved in water when their concentration is sufficiently low, but if the concentration exceeds a certain limit they form coordinated molecular or ionic aggregates dispersed in the solution, as shown in Fig. 9.1.

The hydrocarbons are hydrophobic. Since the surface tension, γ_{hc}, of the hydrocarbons is 22 mJ/m^2 (erg/cm^2) and the dispersion contribution to the total surface tension of water, γ_w^d, is 21.8 mJ/m^2, the work of adhesion between an alkyl chain and water is given by (see Eq. 8.11)

$$W^{adh} = 2(\gamma_{hc}\gamma_w^d)^{1/2} \simeq 44 \text{ mJ/m}^2 \text{ or } 44 \text{ erg/cm}^2 \ .$$

This is, therefore, about the same as the work of cohesion (= $2\gamma_{hc}$) of an alkyl hydrocarbon. On the other hand, the cohesion of water is $2\gamma_w = 146$ mJ/m^2. Therefore, the hydrocarbons are insoluble in water. An amphipathic solute, however, is soluble in water because of its hydrophilic head. This solubility introduces dis-

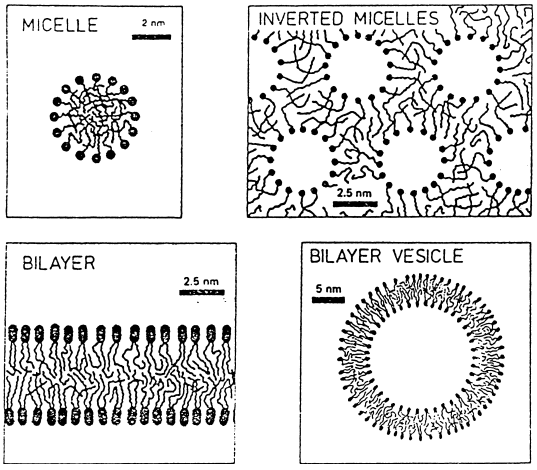

Fig. 9.1 Various aggregates of amphiphilic molecules. Amphiphilic substances carry hydrocarbon chains (Israelachvili, 1991, with permission from Academic Press).

crete molecules containing a hydrocarbon chain into an aqueous environment, creating a region of lower density of water molecules around the hydrocarbon. Accordingly, around this region, like a free surface of water, there is a reduction of the number of nearest neighbors and of possible bonding states among water molecules. This implies a decrease in entropy of water and hence an increase of free energy of the system. This entropy reduction seems to be manifested by the ordering of water molecules near the hydrocarbon chains (Hühnerfuss and Alpers, 1983; Takeo, 1993). The adsorption behavior of amphipathic solutes in aqueous solution causes entropy changes within the water, rather than a specific change in the property of the solutes. The experimental results of Shinoda (1977) with the solubility of benzene in water suggest a strong dependence of this behavior on temperature.

The interfacial activity is due to a relative difference in the work of cohesion between a solute and a solvent. This activity is missing if the work of cohesion is the same for them. The surface activity of hydrocarbons in an aqueous medium continues to exist by lengthening the chain, as being observed in detergency, antibiotic action, hemolytic action, and emulsification. The solubility of hydrocarbons with hydrophilic heads in water is maximum around the chain length of sixteen carbon atoms, above which it decreases rapidly, allowing only a few molecules in the solution. The solubility depends also on the concentration and causes spontaneous association (self-assembly) of such amphipathic molecules, to form artificial membranes, bilayers, colloidal particles (micelles and vesicles, see Sec. 2.3), and biological membranes. There are many thermodynamic treatments of the formation, including Hall and Pethica (1967) based on Hill's procedure on small systems (Hill (1964), Tanford (1980), Mitchell and Ninham (1981), and Puvvada and Blanckstein (1990)).

The Tanford model follows the thermodynamic description of self-assembly as a kinetic equilibrium between the monomers and the aggregates, instead of as a phase separation.

Let us consider the equilibrium model of the self-aggregation. For simplicity, consider the self-assembly in the form of (spherical) micelles, such that they always appear in an equal size of aggregation number N (N molecules or monomers in each micelle). Of course, N could be any number and various values of N are possible to coexist simultaneously. But theoretical treatments predict nearly the same size and, in fact, the almost equal size is more or less in accord with observations and the following geometrical consideration. Namely, the area of the interface of a micelle with water will be occupied by the hydrophilic heads, each of which has a definite size, and the hydrocarbon parts must just fill the internal volume by themselves. If so, the model of the micelle formation is represented by

$$NA_1 \rightleftarrows A_N \tag{9.1}$$

for which the equilibrium constant is given by

$$K = c_N / c_1^N \tag{9.2}$$

where c_N and c_1 are concentrations (activities or mole fractions if the concentration is low) of the micelle and the monomer, respectively.

In order to obtain the free energy per monomer of a micelle, it is desirable to express the concentrations in a different way. We denote by X_N the total mole fraction of amphipathic molecules in micelles of size N, so that $X_N = Nc_N$ and Eq. 9.2 yields

$$K = X_N / N X_1^N \tag{9.3}$$

Then, the change of the standard Gibbs free energy in the formation of a micelle of size N is given by

$$\Delta G^0 = -k_B T \ln K = -k_B T \ln(X_N/N) + N k_B T \ln X_1 \tag{9.4}$$

We note that in order for the micelles to be spontaneously formed the free energy must decrease in the formation, i.e., $\Delta G^0 < 0$. In fact, K must be very large compared with unity in order for a noticeable self-assembly to occur (Exercise 9.1). Namely, if K is large, when the total number of molecules in the solution exceeds some value, the excess molecules are brought into assembly and the monomer concentration remains at the value. If $K = 1$, $\Delta G^0 = 0$ and the molecules remain as monomers. The value of K or ΔG^0 is the key point of the self-assembly.

Now, in terms of the change of the standard chemical potentials, μ_N^0-μ_1^0, Eq. 9.4 can be expressed as

$$N(\mu_N^0 - \mu_1^0) = -k_B T \ln(X_N/N) + N k_B T \ln X_1 \tag{9.5}$$

Therefore, we have

$$\mu_N^0 + (k_B T/N) \ln(X_N/N) = \mu_1^0 + k_B T \ln X_1 \tag{9.6}$$

The chemical potential, μ_N, for the micelle must be equal to that, μ_1, for a monomer in equilibrium, i.e.,

$$\mu_N = \mu_1 \tag{9.7}$$

Comparing this with Eq. 9.6, we can write

$$\mu_N = \mu_N^0 + \frac{k_B T}{N} \ln \frac{X_N}{N} \tag{9.8}$$

For the spontaneous micelle formation, $\mu_N^0 < \mu_1^0$.

Experimental evidence for the presence of micelles in aqueous solutions of amphipathic solutes is obtained from measurements of the osmotic pressure, the lowering of the vapor pressure, the elevation of the boiling point, the depression of

the freezing point, and the change of the electrical conductivity. Each of these, in general, shows a rapid change of the measured values when the concentration of the solutes is varied, irrespective of whether the solutes are ions, molecules, macromolecules, micelles, or vesicles.

Comparing Eqs. 9.4 and 9.5, K is found to be determined by the difference of the standard chemical potentials. The value of μ_N^0 depends on the structure of the micelles. It is contributed by two parts: one is due to the interaction of the hydrocarbon tails of the amphipathic molecules inside the micelle and another comes from their hydrophilic head groups at the interface with surrounding water. The hydrocarbon chains are in a state inside the micelles and contribute a chemical potential $g(T,l)$, where l is the length of the hydrocarbon chain. The attraction among hydrocarbons mainly comes from the entropy effect due to the ordering of water molecules (called as a hydrophobic attraction) causes a surface tension ($\gamma \sim 50$ erg/cm^2) at the interface. We assume that γ does not depend on the curvature of the interface. For amphipathic molecules the presence of hydrophilic head groups at the interface cannot be ignored and reduces the surface tension as low as 20 erg/cm^2 (Jönsson and Wennerström, 1981). Another effect of the head groups is that they remain in contact with water molecules at the interface and they repel head groups each other. However, the repulsive contributions to the free energy are too complex to be theoretically formulated (Puvvada and Blankstein, 1990).

We consider the following simple example of unionized molecules as an illustration. We assume that the dielectric constant of water at the interface is the same as the bulk value ($\varepsilon_w \sim 80$, but must be much smaller at the interface) and that the head groups form an electrostatic double layer. Further, we assume that the head groups have the electric dipole moments of $e{\cdot}d$ (charge·separation) per head, which are oriented perpendicularly to the interface, and form a double layer of separation d at the interface. If the surface area of A_m is occupied by each head, the charge on the double layer is e per area A_m and the electrostatic energy is $e^2 d/(2\varepsilon_0 \varepsilon_w A_m)$, which will be written as D/A_m in the following. Since μ_N^0 is per molecule of the micelle, we then have

$$\mu_M^0 = \gamma A_m + \frac{D}{A_m} + g \tag{9.9}$$

Here, the water molecules at the interface are considered to be randomly oriented, although the arrangement is supposed to be ordered and the above model must be accordingly modified. We must know that the value of the surface area A_m per molecule cannot be easily found (Takeo, 1993). We note that, whatever the mechanism may be, the repulsive part of the energy has the same general form of D/A_m in the first approximation, although the content of the constant D must be altered accordingly.

On the other hand, μ_1^0 is for the molecules in the dispersed state. The electrostatic energy of the dipole ($e{\cdot}d$) can be ignored compared to D/A_m under a reasonable assumption that $d^2 \ll A_m$ (Exercise 9.3). Hence, the free energy is contributed

only by the hydrophobic interactions between the hydrocarbons and water, which may be denoted by g'. This g' corresponds to the above g of a micelle. Stigter (1975) estimated that

$$g' - g \approx n \cdot 187 \text{ J/mole of } CH_2 \text{ group} \tag{9.10}$$

where n is the number of carbon atoms in the hydrocarbon chain, excluding the C atom at the free end. (At the free end, the energy difference g'–g = 500 J/mole of CH_3 group.) This implies that if a hydrocarbon chain consists of sixteen carbon atoms in total,

$$g' - g = 5.5 \cdot 10^{-14} \text{ erg/molecule}$$

Suppose that a spherical micelle of aggregation number N has radius r. For the purpose of simplification we assume that

$$A_m = 4\pi r^2/N = 3v/r \tag{9.11}$$

where v is the volume of the molecule. Therefore, we have

$$\mu_N^0 \mu_1^0 = \gamma\left(A_m + \frac{A_d^2}{A_m}\right) + g - g' \tag{9.12}$$

where A_d is defined by

$$A_d^2 = \frac{D}{\gamma} \tag{9.13}$$

Since μ_N^0–$\mu_1^0 = 2\gamma A_d + (\gamma/A_m)(A_m - A_d)^2 + g - g'$ from Eq. 9.12, value of μ_N^0–μ_1^0 is minimum when $A_m = A_d$. Thus, ΔG^0 is minimum and K is maximum if $A_m = A_d$. This value of A_m will be later called the optimal size A_0.

From Eq. 9.11, $A_m = (4\pi(3v)^2/N)^{1/3}$, so that A_m depends on N. We denote by M the value of N when $A_m = A_d$ and ΔG^0 is minimum. This value of M is independent of the total concentration of the molecules. If N is either very large or very small compared with M, the value of ΔG^0 can be positive, since g–g' is given by Eq. 9.10, and micellization does not occur. Thus, stable micelles occur only within a relatively narrow region of the size (Fig. 9.2).

If $N = M$, μ_M^0–$\mu_1^0 = 2\gamma A_d + g - g'$. Therefore,

$$\mu_N^0 - \mu_M^0 = (\gamma/A_m)(A_m - A_d)^2 \tag{9.14}$$

If surfactants of a micelle are ionic, the electrostatic repulsive interaction between the head groups on the surface makes the micelle unstable, unless the interaction is moderated to a considerable extent. Usually, a large proportion of the

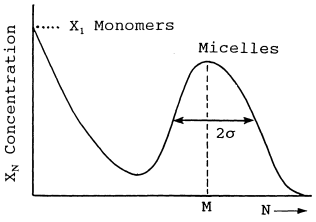

Fig. 9.2 Distribution of molecules as a function of aggregation number N.

counterions ($\sim$50 to 80 percent) are strongly bound to the surface. The ion binding is exactly analogous to the formation of a Stern layer (see Sec. 10.2.3). See Wennerstrom and Lindman (1979) for the summary.

9.2 The Critical Micelle (or Micellization) Concentration (CMC)

The relative behavior of X_1 and X_N as the total concentration increases is treated in Exercise 9.4. This behavior is depicted in Fig. 9.3. It solely depends on the value of the equilibrium constant, K. When $\mu_N^0 - \mu_1^0$ is minimum at $N=M$ and negative, we write that

$$(\mu_M^0 - \mu_1^0)/k_B T \equiv -\alpha \ , \quad (\alpha > 0) \tag{9.15}$$

From Eq. 9.5, we have

$$X_M = M\{X_1 e^{\alpha}\}^M \ . \tag{9.16}$$

The value of M is in the range of 40 to 140.

For small concentration ($c=X_1+X_M$, in mol fraction), X_1 is small and $X_1 e^{\alpha} \ll 1$, so that X_M/M is small for any value of M. If the concentration increases, X_M/M increases. But since

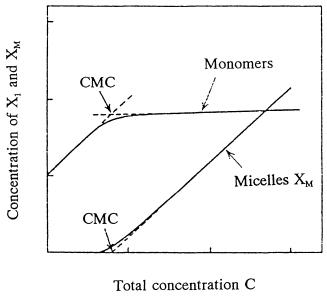

Fig. 9.3 Monomer and micelle concentration as a function of total concentration (mol fraction).

$$X_1 = (X_M/M)^{1/M} e^{-\alpha} \tag{9.17}$$

noting that $X_M/M = c_M$ can never exceed unity, once c_M gets closer to unity X_1 approaches $e^{-\alpha}$ as a limit. This sets the critical micelle (or micellization) concentration (*CMC*):

$$(X_1)_{N=M} = CMC = e^{-\alpha} = \exp\{(\mu_M^0 - \mu_1^0)/k_B T\} \tag{9.18}$$

Since $\mu_M^0 - \mu_1^0 = 2\gamma A_d + g - g'$ at $N = M$, we have

$$\begin{aligned} \ln CMC &= (2\gamma A_d + g - g')/k_B T \\ &= [2\gamma(36\pi v^2/M)^{1/3} + g - g']/k_B T \\ &= D_1/M^{1/3} + D_2 \end{aligned} \tag{9.19}$$

Although the model is crude, this result agrees very well with the experiments (Israelachvili et al., 1976). It is suggested that $g' - g$ has the largest value among other terms in Eq. 9.12 and it is proportional to the number of carbon atoms, n, in the hydrocarbon chain. In fact, according to Mukerjee and Mysels (1971),

$$\ln[CMC \text{ in M}] = 4.01 - 0.65 \cdot n\,, \quad (n \leq 14) \tag{9.20}$$

for aqueous solutions of a homologous series of sodium soaps without adding any electrolyte. *CMC* seems to be also related with *HLB* (Eq. 12.3).

Equation 9.14 suggests that if μ_N^0 is a minimum at $N = M$, we can approximately express, for $N \sim M$, as

$$\mu_N^0 - \mu_M^0 = C(N - M)^2 \tag{9.21}$$

with a constant, C. Then, X_N approximately distributes as Gaussian about M with standard deviation, σ, in N given by

$$\sigma^2 = k_B T/2CM \tag{9.22}$$

Zana (1995) noted the established experimental observation that $\sigma^2/\langle N\rangle$ is an approximately constant value of 2 and

$$\gamma = 0.0293\langle N\rangle/\sigma^2 \text{ Jm}^{-2} \tag{9.23}$$

Therefore, the surface tension γ is in the range 15 to 20 mJm^{-2}.

It is easy to see that the osmotic pressure, surface tension, turbidity, solubilization, etc. of a solution undergo abrupt changes in concentration dependence at *CMC*.

9.3 Bilayers and Vesicles

As a kind of the self-assembly behavior of amphiphilic molecules, lipids form bilayers, as discussed in Sec. 2.2.2. Most biological membrane lipids are double-chained phospholipids or glycolipids with 16 to 18 carbons per chain. One of the chains is unsaturated, so that the chains exhibit a good fluidity. The lipids are strongly hydrophobic and have an extremely low *CMC* (10^{-6}–10^{-10} M), so that almost all of them in water go into a form of self-aggregation with polar head groups in water. However, since the relative size of the polar head is small compared to the body of hydrocarbons, when lipids aggregate, they cannot form a spherical micelle. Instead, they form a monolayer at the water surface or a bilayer in the bulk water. Here, to compensate the small head group, a portion of the hydrocarbons next to the head group is bent and located inside the water. Hence, the surface area of the monolayer or the bilayer is larger than the cross-sectional area of the head group. This surface structure and the fluidity of the lipid hydrocarbon chains are important for an ionic transport through the biological membrane. In addition, because of the strong hydrophobicity of lipids, $\mu_N^0 - \mu_1^0$ is negatively large and any lipid in the bilayer hardly leaves the bilayer under a thermal motion. Self-aggregation process is highly dynamic. Molecules involved in the process make constant thermal motion within the aggregates and exchange monomers with the solution (Pfeiffer et al., 1989). But those lipids must remain in the bilayer at least few hours because of the negatively large $\mu_N^0 - \mu_1^0$ (Israelachvili, 1991, p. 375). In addition, there is a flip-flop of a lipid by passing the polar head through the hydrocarbon region from one side to another of the bilayer. But the activation energy is higher than that for a lipid to leave the membrane.

As shown in Fig. 9.1, a bilayer often forms a closed spherical shape, enclosing solvent inside. This is called a vesicle. The bilayer in this form can avoid energetically unfavorable edges at a finite, instead of infinite, aggregation number. This structure without free edges is also entropically favorable. The possible size of the vesicle is understood in terms of the geometrical packing of lipids. This approach gives a good result as described below.

9.4 Geometric Packing or Size of a Hydrocarbon Chain in a Micelle

In a spherical micelle, the radius r cannot exceed the maximum effective length, l_c, of hydrocarbon chains, which form the micelle. If v denotes the volume of a hydrocarbon chain inside the micelle of radius r, then the condition yields that $(4\pi r^3/3)/(4\pi r^2) = v/A_0 = r/3 < l_c/3$, i.e., $v/A_0 l_c > 1/3$, where A_0 is the optimal surface area per molecule ($A_0 = A_d$, Eq. 9.13). According to Tanford (1980), a saturated hydrocarbon chain with n carbon atoms has

$$l_c \leq 0.145 + 0.127 \cdot n \text{ nm} = 1.67 \text{ nm} \quad \text{with} \quad n = 12$$

$$v \approx (0.0274 + 0.0269 \cdot n) \text{ nm}^3 = 0.350 \text{ nm}^3 \quad (n = 12)$$

Thus, for the 12-carbon chain sodium dodecyl sulphate surfactant,

$$A_0 > 3v/l_c = 0.63 \text{ nm}^2 \quad \text{and} \quad M < 4\pi l_c^2/A_0 = 56$$

These values agree with experimental observations. Thus, the geometrical packing consideration seems to be effective.

By applying the above procedure, we obtain the minimum size r_m of a vesicle (Israelachvili et al., 1976):

$$r_m = l_c \left[\frac{3 + \sqrt{3(4\beta - 1)}}{6(1 - \beta)} \right], \quad \beta = \frac{v}{A_0 l_c} \tag{9.24}$$

This also gives a good result. For egg yolk lecithin vesicles, $r_m \approx 11$ nm.

Extending the consideration of the packing parameter, $v/A_0 l_c$, to other shapes of micelles and other aggregates, we have the conditions:

Spherical micelle	$v/A_0 l_c < 1/3$
Cylindrical micelle	$1/3 < v/A_0 l_c < 1/2$
Vesicle or bilayer	$1/2 < v/A_0 l_c < 1$
Inverted micelle	$1 < v/A_0 l_c$

(9.25)

9.5 Spectroscopic Technique for Investigating Micelles

As mentioned above, the direct methods are possible for observing the presence of micelles in aqueous solutions of amphipathic solutes. These include measurements of the osmotic pressure, the lowering of the vapor pressure, the elevation of the boiling point, and the depression of the freezing point. But there are other methods which require an additive. For instance, in spectroscopic techniques, either optical absorption or emission of light from some probe molecules (dye or fluorescent additives) may be used (Mukerjee and Mysels, 1971). The method without an additive is preferable as its presence can affect the self-assembly.

9.5.1 Methods for Determining the CMC

The solution of ionic amphipathic solutes shows a discontinuity at the *CMC* in the variation of specific electrical conductivity with respect to the total concentration. This is the simplest experimental technique in determining the *CMC*.

The most popular optical method is to measure turbidity. This is to use the fact that the intensity of the scattered light depends on the square of the volume of particles (Eq. 6.1). Micelles scatter more light than the monomers and the scattered intensity sharply increases at the *CMC*.

A surface tension provides another method of determining the *CMC*. For a two-component system, the surface tension varies with the concentration (or activity), c_2, of the solute according to Eq. 2.27. Amphiphilic molecules are readily adsorbed into the surface phase. Once micelles form in significant quantities, the monomer concentration increases only slightly with increase of the total concentration. Therefore, as pointed at Eq. 2.27, the plot of the surface tension versus the concentration first shows an abrupt decrease but ceases to do so at the *CMC*, which is around 10^{-3} or 10^{-2} *M* for a detergent.

9.5.2 Methods for Determining the Aggregation Number

9.5.2.1 Scattering Method

Any method for determining particle sizes is applicable for micelles, including turbidity, photon correlation, x-ray and neutron small angle scattering, etc.

We have discussed that the measurement of the turbidity (Eq. 6.4) can give a mass-averaged particle mass. If the molecular weight of the molecules which form micelles is known, then the turbidity can yield the aggregation number.

As pointed out in x-ray scattering, a micelle has a hydrophobic core and a hydrophilic shell. A strong scattering peak will appear due to the interference between the x-rays scattered by the core-shell structure. This peak must be accordingly interpreted in terms of a correct model of the structure.

9.5.2.2 Fluorescence Method

Micelles can solubilize relatively large amounts of sparingly water-soluble compounds. If fluorescent probe molecules and quenching molecules are such compounds, they are well associated with the micelles for a long time. If there is no quenchers, the fluorescence from the probes can be observed (the intensity: I_0). (There may be some absorption or scattering of the emitted fluorescent light in the system.) If one or more quenching molecules are present in a micelle and the quenching process is much faster than the emission lifetime of the probe, the micelle does not participate in the fluorescence. The number of micelles which do not contain any quenchers is easily found since it is proportional to $\exp(-c_q/c_M)$ according to Poisson's statistics, where c_q and c_M are concentrations of the

quenchers and the micelles, respectively. Therefore, the intensity will obey the relation (Turro and Yekta, 1978):

$$I = I_0 \exp[-c_q/c_M] \tag{9.26}$$

However, how the quenchers quench the fluorescence is not quite known.

Now, $c_M = (c_T - CMC)/\langle N \rangle$, where c_T is the total concentration of amphiphilic molecules and $\langle N \rangle$ is the mean aggregation number. Thus,

$$\ln(I_0/I) = [\langle N \rangle/(c_T - CMC)] \cdot c_q \tag{9.27}$$

Therefore, if we change c_q in the experiment, we can determine $\langle N \rangle$.

This method is checked for accuracy by Almgren and Löfroth (1980) if the aggregation number is less than 120.

9.5.2.3 Time-resolved Fluorescence Method

Suppose that the system is exposed to a pulsed (laser) light. If both fluorescent probes and quenching molecules are present in micelles, then the emitted fluorescent light will decay as follows (Almgren and Löfroth, 1980),

$$I(t) = I(0)e^{\left[-\frac{t}{\tau_0} + \frac{c_q}{c_M}(e^{-k_q t} - 1)\right]} \tag{9.28}$$

where τ_0 and k_q are the lifetime of the upper state for the fluorescent emission process without a quencher and the quenching rate constant in micelles, respectively.

Depending on weather $t \ll$ or $\gg 1/k_q$, Eq. 9.28 is reduced to

$$\ln\frac{I(t)}{I(0)} = -\left(\frac{1}{\tau_0} + \frac{c_q k_q}{c_M}\right)t \quad \text{or} \quad -\frac{t}{\tau_0} - \frac{c_q}{c_M} \tag{9.29}$$

respectively. Thus, by changing the quencher concentration, c_q, we can determine various parameters including average aggregation number, $\langle N \rangle$.

One of the advantages of this method is that Eq. 9.29 does not depend on the mutual interactions among micelles. If there is a scattering, it remains in the same relation during the observation. Therefore, this time-resolved method can be used over a much wider range of micelle sizes.

9.5.2.4 Other Methods for Sizing

Ultrafugation or sedimentation combined with density and diffusion measurements can be used for the micelle sizing (Courchene, 1964). If micelles are ionic, the

electrokinetic effects affect the result unless these are swamped out by salts (Anacker et al., 1964).

The membrane osmometry is also important. See Birdi (1972) for the experimental details.

9.6 Micellar Dynamics

As mentioned earlier in Sec. 9.3, micelles are constantly forming and dissociating usually on a time scale of μs to ms range. But the time scale for the similar phenomena in bilayers is much longer. The dynamical micellar behavior has been studied mainly by fast relaxation methods in temperature jump, pressure jump, ultrasonic absorption, shock-tube methods, etc. In all of these jumps the thermal equilibrium is broken, and relaxation follows. How fast it returns to equilibrium can be observed by measuring, as a function of time, the electric conductivity, turbidity, and light scattering. The time response of about 10 μs to 1 ms can be easily observed.

If the period of the applied ultrasonic oscillation is much longer than the relaxation time, the micellar system can follow the oscillation and the ultrasonic wave is not damped. But, when the period and the relaxation time become nearly the same on increasing the frequency, the ultrasonic absorption occurs by the energy loss due to the micellar forming and dissociating process. If so, the damping can be observed by the pulse radiolysis method in the range of 10^{-8} to 10^{-5} s.

These measurements consistently disclose two distinct relaxation times. For instance, sodium dodecylsulphate (SDS) species has two relaxation times of about 10^{-5} and 10^{-3} s and the theory of Aniasson and Wall (1974) has been used for the analysis (see also Aniasson et al., 1976). However, there are some differences of theoretical opinion on micelle formation (Kahlweit, 1981).

9.6.1 Fast Relaxation Time, τ_1

The reaction involved is considered as the following monomer exchange.

$$A_{N-1} + A_1 \rightleftarrows A_N \tag{9.30}$$

The reaction rate (forward) for recombination is denoted by k^+ and that (backward) of dissociation by k^-. A pulse radiolysis study (Almgren et al., 1979) has confirmed that the monomer exchange is responsible for the first relaxation time of SDS.

The size, N, of micelles distributes around the optimal aggregation number M. The monomer exchange occurs within this distribution and monomers. For sim-

plicity, we assume that the reaction rates do not depend on N. Like Eq. 3.7 in the nucleation case, we have

$$\frac{\partial c_N}{\partial t} = k^+ c_{N-1} c_1 + k^- c_{N+1} - k^+ c_N c_1 - k^- c_N \tag{9.31}$$

We denote by c_N^* the equilibrium concentration. In equilibrium the exchange reaction, Eq. 9.30, can be written as

$$k^+ c_{N-1}^* c_1^* = k^- c_N^* \tag{9.32}$$

where k^- is in the range of about 10^9 to $10^6\ s^{-1}$ for alkyl sulphate NaC_6SO_4 to $NaC_{14}SO_4$, respectively, and k^+ is about $10^9\ M^{-1}\ s^{-1}$ for the alkyl sulphates.

We define the relative deviation of the concentration c_N of the size, N, from the equilibrium value, c_N^*, by

$$y_N = (c_N - c_N^*)/c_N^* \tag{9.33}$$

Then, if we use the approximations:

$$y_{N\pm1} = y_N \pm \frac{\partial y_N}{\partial N}\ ,\quad c_{N\pm1}^* = c_N^* \pm \frac{\mathrm{d}c_N^*}{\mathrm{d}N} \tag{9.34}$$

where the partial differentiation is due to the fact that y_N is function of N and t, we can rewrite Eq. 9.31 as follows

$$\frac{\partial y_N}{\partial t} = k^- \left[\frac{\partial^2 y_N}{\partial N^2} - y_1 \frac{\partial}{\partial N}\left(y_N - \frac{\partial y_N}{\partial N}\right) + \frac{1}{c_N^*}\frac{\mathrm{d}c_{N+1}^*}{\mathrm{d}N}\left(\frac{\partial y_N}{\partial N} - y_1(1+y_N)\right)\right] \tag{9.35}$$

This may be solved under the assumption that c_N^* distribute according to a Gaussian distribution with the variance σ^2 (Eq. 9.22). The boundary conditions to be used are that the micelle concentrations do not vanished only around the optimal number M. The solution is cumbersome. The result of Aniasson and Wall (1974) shows that when c_T is the total concentration the average deviation y_N decays with the relaxation time, τ_1, which is given by

$$\frac{1}{\tau_1} = \frac{k^-}{\sigma^2} + \frac{k^-}{\langle N\rangle}\left(\frac{c_T}{c_1^*} - 1\right) \tag{9.36}$$

where $\langle N\rangle = M$, the optimal number. If c_1^* is equal to the value of the *CMC*, $1/\tau_1$ may be plotted against $(c_T/c_1^* - 1)$ to obtain a straight line, the slope of which gives $k^-/\langle N\rangle$. Kato et al. (1995) suggested that non-ionic surfactants might have two fast relaxation times.

9.6.2 Slow Relaxation Time, τ_2

The slower relaxation event has been identified by Muller (1977) with the following sequence of (N–1) steps.

$$A_1 + A_1 \rightleftarrows A_2\ ,\ \ A_2 + A_1 \rightleftarrows A_3, \cdots\ ,\ \ A_{N-1} + A_1 \rightleftarrows A_N \tag{9.37}$$

This model implies that the monomers A_1 released by the dissociation of a micelle of size, N, break the equilibrium value c_1^* as well as c_N^*. The recovery from this perturbation is considered to occur by the process expressed by the sequence of Eq. 9.37. Namely, excess monomers pass through the sequence of growing i and, thus, form a flux in the population space. The monomers have a probability of initiating the sequence at any stage of aggregation. However, the sequence is more likely initiated at smaller sizes, because the concentrations of the aggregates are small in the intermediate sizes. Then the monomer flux must go, in the population space, through the region of intermediate sizes whose concentrations are smallest (Fig. 9.2) and the reaction rates are accordingly small. This region is the rate-determining of the relaxation process. This region can be vaguely defined as located between the aggregation numbers, s_1 and s_2. Then, the set of rate equations (such as Eq. 9.31) between these sizes are solved to obtain the flux in this region. Intuitively, the time required for the stepwise growing aggregate to pass through this region in the population space is the sum of the time required for each step. Therefore, we define

$$R = \sum_{s=s_1}^{s_2} \frac{1}{k_s^- c_s^*} \tag{9.38}$$

where the rate constant, k_s^-, now depends on the aggregation number s. Because of Eq. 9.32 R is dependent on c_1^*, so on CMC. The dependence will be complex, if the monomers are ionic and cause the redistribution of free counterions. After all, if non-ionic, the over-all stepwise processes are represented by a single relaxation time, τ_2. According to Aniasson et al. (1976)

$$\frac{1}{\tau_2} = \frac{\langle N \rangle^2}{R c_1^* \left[1 + \frac{\sigma^2}{\langle N \rangle}\left(\frac{c_T}{c_1^*} - 1\right)\right]} \tag{9.39}$$

The relaxation time is, of course, related to k^+ but for larger alkyl chain the dependence is less important compared to k^-.

Equation 9.39 shows that τ_2 increases as c_T increases. If c_T is much larger than *CMC*, however, τ_2 decreases after passing through its maximum value. This behavior is theoretically understood as due to coagulation and dissociation among micelles (Faetibold and Watson, 1995).

Equation 9.39 does not take into account the redistribution of free counterions and must be modified, if surfactants are ionic (Chan and Kahlweit, 1977). It predicts an appearance of a maximum in the plot of $1/\tau_2$ against c_T, while if non-ionic τ_2 should change monotonically, in good agreement with observations.

9.6.3 Residence Time of Micelles

The residence time of small molecular substances, such as those commonly used as probes, is an important factor in consideration when interpreting dynamic results such as fluorescence quenching behavior. Since most hydrophobic probes have residence times that are longer than their fluorescence lifetimes, the quenching techniques are not suitable for determining probe residence lifetimes in micelles.

The idea of the residence time is applicable to the molecules of a micelle. The probability per unit time of changing the aggregation number by one with a micelle of the aggregation number, N, is $k^-+k^+c_1$ in the present model. Since $k^-=k^+c_1$ in equilibrium, the time, during which a given micelle does not change its aggregation number, or the residence time is $1/(2k^-)$. Thus, in a micelle of an aggregation number, N, the probability per unit time of one of the molecules to leave the micelle is $(k^-+k^+c_1)/N$. Therefore, the average residence time of a molecule in the micelle is $N/(2k^-)$. This process can also be understood in the scheme of a nuclear α-decay. The escape of a molecule of the micelle must occur by overcoming the potential barrier of activation energy, ΔE, after it collides with the micellar wall. The collision time, τ_0, is of the order of 10^{-9} to 10^{-7} s. The activation energy, ΔE, is about $(\mu_1^0-\mu_N^0)$ of Eq. 9.5. Thus, since $\tau_R \approx \tau_0 \exp(-\Delta E/k_B T)$, by using Eq. 9.18, the residence time is given by *CMC* (mole fraction) as

$$\tau_R \approx N/(2k^-) \approx \tau_0/CMC \tag{9.40}$$

In aqueous solutions, $CMC = [CMC \text{ in M}]/55.5$.

On the other hand, the transition time of a micelle is defined by the time required for a micelle to change its aggregation number from N' to N''. The residence time is the transition time for $|N'-N''|=1$. If $N' \equiv N$ and $N'' \equiv 1$, the average transition time is given by, according to Aniasson (1985),

$$\langle t \rangle = \frac{N\tau_2}{1+\frac{c_1^*}{c_T}+\frac{\sigma^2}{N}} \sim N\tau_2 \tag{9.41}$$

This is the time required for the micelle to almost completely disintegrate or to completely replace the molecules. For SDS ($N \sim 100$), $\langle t \rangle$ is about 70 ms.

Exercises

9.1 Consider a liquid consisting of a mixture of molecules A and molecules B in equal amount. If the molecules are randomly dispersed, an A molecule will have, with equal probability, both molecule A and molecule B as nearest neighbors and similarly for a B molecule. Thus, AB combinations are more probable. But if the molecules are associated to their own molecules, AA and BB combinations are more probable. Show that the molecular combination is energetically favored in the form of association, whenever the work of cohesion for A molecules and B molecules are different, irrespective of which one, W_{AA} or W_{BB}, is larger. (Remark: Consider two A molecules and two B molecules. If associated, we have A-A and B-B combinations. If dispersed there are two A-B's. From Eq. 8.9, the difference in the energies of the system in the two alternative cases is $W_{\text{associated}}-W_{\text{disperse}}=-A^2-B^2+2AB=-(A-B)^2$. Consider a larger sample.)

9.2 Consider the reaction represented by Eq. 9.1. Then, show that the change in the Gibbs free energy is given by Eq. 9.4.

9.3 Find the electrostatic energy of an electric dipole (moment: $e{\cdot}d$) immersed in water ($e^2/(4\pi\varepsilon_0\varepsilon_w d)$).

9.4 Consider the reaction of Eq. 9.1 (N is fixed, so that there are only monomers and clusters of fixed aggregation number N). Then, the equilibrium constant is given by Eq. 9.2. Express the total concentration ($c=\sum X_N$) of solute molecules in terms of c_1 and c_N. For a large value of K ($=10^{80}$), plot c_1 against various values of the total concentration ($c=10^{-5}$, 10^{-4}, and 10^{-1}) for $N=10$, 20, and 30. (Hint: Find a relation between K, N, c, and X_1. Then, find a suggestive behavior of X_1 for large c.)

9.5 Using Eq. 9.20, determine the contribution from each additional carbon atom in the chain to the free energy on micellization.

9.6 Using the relation, Eq. 9.21, show that the size (N) distribution of micelles is Gaussian.

9.7 Establish the set of relations of Eq. 9.25.

9.8 Derive Eq. 9.28.

9.9 Show that the probability per unit time of changing the aggregation number by one is $k^-+k^+c_1$ for any micelle (see Sec. 9.6.3).

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